EQUILIBRIUM STRUCTURE OF PIPERIDINE

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In order to determine an accurate equilibrium structure for the equatorial form of piperidine, $C_5H_{11}N$, microwave transitions and ground state rotational constants are reported for the ^{13}C and ^{15}N isotopologues measured in natural abundance. These rotational constants along with those of the parent and ND species were used together with vibration-rotation constants obtained from a cubic force fields calculated at the B3LYP/cc-pVTZ and MP2/cc-pVTZ levels of theory to derive a semiexperimental (SE) equilibrium structure. However, the rotational constants of the CD deuterated species are not available, and there are many small Cartesian coordinates. Furthermore, piperidine is an oblate top. Quite generally, there is a large rotation of the principal axis system upon isotopic substitution in oblate tops that may considerably reduce the accuracy of the SE structure. For these reasons, the mixed estimation method was used. In this method, internal coordinates from good-quality quantum chemical calculations (with appropriate uncertainties) are fitted simultaneously with moments of inertia of the full set of isotopologues. In order to have predicates as accurate as possible, the geometry was optimized at the MP2 and CCSD(T) levels of theory using Dunning basis sets up to quadruple-zeta quality. This combination of experimental rotational constants and high-level ab initio calculations allowed us to determine an accurate equilibrium structure.